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14. ABSTRACT Solid hydrogen doped with energetic impurities may form the basis for HEDM to be used in rocket propulsion. A key research priority has been to investigate the equilibrium properties of a boron impurity and of an aluminum impurity trapped in solid para-hydrogen. The simulation methods used in the study allow us to take into account the quantum nature of the HEDM in question. Using classical molecular dynamics simulations to evaluate these equilibrium properties would predict qualitatively incorrect results for low temperature solid hydrogen, because of the highly quantum nature of the hydrogen matrix. The immediate goal of our group's Air Force-supported low temperature HEDM research program is to understand from large-scale computer simulation the differences in the equilibrium properties of the HEDM when the doped impurity is aluminum, and to assess the effects of anisotropic interactions between the impurity and the p _{H2} molecule. In low temperature hydrogen HEDM, quantum effects are enormous, so a highly specialized method is required for these demanding computer simulations.					
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AFOSR Final Report

Quantum Simulations of Low Temperature High Energy Density Matter

(Grant # F49620-01-1-0067)

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Objectives:

The properties of high energy density matter (HEDM) were under investigation in our group. Findings are described below.

A. Low Temperature HEDM Simulations

Solid hydrogen doped with energetic impurities may form the basis for HEDM to be used in rocket propulsion. A key research priority has been to investigate the equilibrium properties of a boron impurity and of an aluminum impurity trapped in solid *para*-hydrogen. The simulation methods used in the study have allowed us to take into account the quantum nature of the HEDM in question. We strongly believed that using classical molecular dynamics simulations to evaluate these equilibrium properties would predict qualitatively incorrect results for low temperature solid hydrogen, because of the highly quantum nature of the hydrogen matrix.

The goal of our group's Air Force-supported low temperature HEDM research program was to understand from large-scale computer simulation the differences in the equilibrium properties of the HEDM when the doped impurity is aluminum, and to assess the effects of anisotropic interactions between the impurity and the pH_2 molecule. In low temperature hydrogen HEDM, quantum effects are enormous, so a highly specialized method was required for these demanding computer simulations.

The primary effort over the course of this project was the large-scale simulation of aluminum and boron impurities in *para*-hydrogen at 4K. Significant results were obtained which are summarized in the next section.

Accomplishments/New Findings:

A. Low Temperature HEDM Simulations

As stated earlier, the computer simulation of impurity trapped in solid hydrogen must account for the highly quantum nature of the system. The method used in our group to study this problem is path integral molecular dynamics (PIMD). In PIMD the ensemble of a given number of quantum particles is represented quantum mechanically by a certain set of that number of pseudoparticles. The dynamics were performed on these pseudoparticles and the phase space was properly sampled. This allowed us to obtain correct results for the equilibrium properties of a highly quantum system like the HEDM studied here.

As stated above, an important part of this study was assessing the effect of the anisotropic interactions of the impurity with the pH_2 molecules in the matrix. This directionality in the interaction is due to the fact that aluminum has a singly filled $3p$ orbital in its ground state.

The potential of the Al- pH_2 pair is then described by two degenerate Π states and a Σ^+ state. If the z -axis is taken to be the internuclear axis, then these three states correspond to the three Cartesian orientations of the singly filled p -orbital (p_z for the Σ^+ state and p_x and p_y for the Π states).

We have compared the calculated equilibrium properties of the system with explicit inclusion of the electronic anisotropy of the impurity- pH_2 interaction, and with a simplified potential in which the impurity- pH_2 pair potential is averaged over the three possible orientations of the p -orbital

Insight into the structure of the equilibrated systems is given by the impurity- pH_2 pair distribution functions, $g(R)$. These were calculated for the single site substituted system and for the system containing a defect in the nearest neighbour site of the impurity. The site substituted system showed less structural change than the system with a defect. Shown in Figure 1 are the $g(R)$ s for the case of a aluminium impurity without a defect.

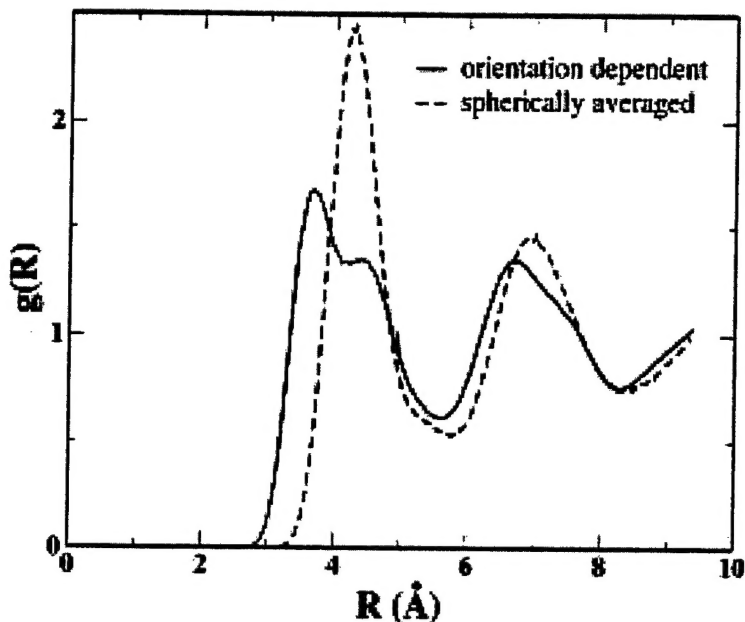


Figure 1

The shift in the profile of the $g(R)$ and the change in the structure of the first peak in Figure 1 implies that there is some structural rearrangement of the lattice in the vicinity of the impurity, and/or rearrangement of the impurity, when the orientation dependent potential is used.

An important part of this project was assessing the effect of the anisotropic interactions of the impurity with the pH_2 molecules in the matrix. This directionality in the interaction is due to the fact that both boron and aluminum have a singly filled p orbital ($2p$ in the case of B and $3p$ in the case of Al).

For example, in the case of the boron, the pairwise interaction of the B in its $2s^2 2p$ electronic ground state with the spherical partner can be described by two degenerate Π states and a Σ^+ state. If the z -axis is taken to be the internuclear axis, then these three states correspond to the three Cartesian orientations of the singly filled p -orbital (p_z for the Σ^+ state and p_x and p_y for the Π states).

For each case, we have compared the calculated equilibrium properties of the system with explicit inclusion of the electronic anisotropy of the impurity- pH_2 interaction, and with a simplified potential in which the impurity- pH_2 pair potential is averaged over the three possible orientations of the p -orbital. Shown in Figure 2 are the $g(R)$ s for the case of a boron impurity with a defect.

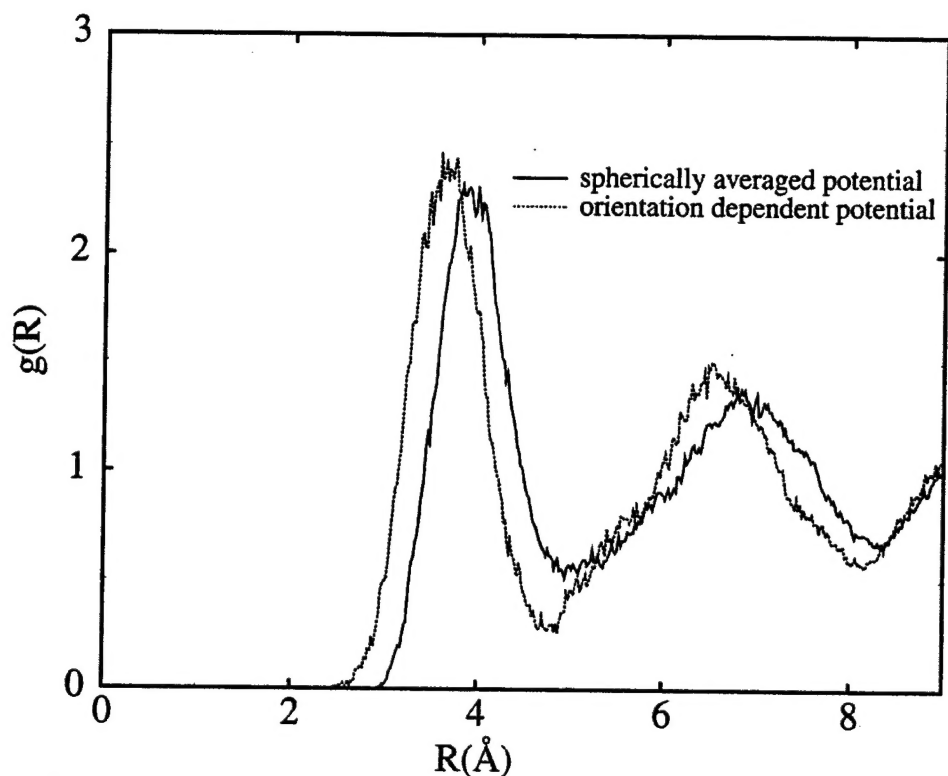


Figure 2

The shift in the profile of the $g(R)$ in Figure 2 implies that there is some structural rearrangement of the lattice in the vicinity of the impurity, and/or rearrangement of the impurity, when the orientation dependent potential is used.

The effect was much more pronounced in the case of an aluminium impurity with a neighboring lattice vacancy. From the Al- pH_2 $g(R)$ in Figure 3, it was apparent that a significant structural rearrangement occurred when the orientation dependent potential was used. The two peaks seen in the profile for the spherically averaged potential split into two when the orientation dependent potential was used. This indicates that the arrangement of the H_2 molecules around the Al is no longer as uniform as in the case of the spherical potential. To gain insight into the cause of the change in the $g(R)$ profiles discussed above, we projected onto the hexagonal plane of the hcp lattice the positions of the Al atom and the 12 nearest neighbor pH_2 molecules for the case of the aluminum impurity with an adjacent defect.

In the site-substituted hcp lattice, six of the nearest neighbors are situated at the vertices of a hexagon in the xy plane, three additional pH_2 molecules are located at the vertices of an equilateral triangle above the xy plane, and the final three pH_2 molecules are at the vertices of an equilateral triangle below the xy plane. Presented in figure 4 is projection obtained using the spherically averaged potential. The origin is defined by the initial hcp position of the Al atom. The filled circles and the filled triangle are the positions of the ideal hcp lattice sites. The squares are the averaged centroid positions of the pH_2 molecules. The open triangle is the averaged centroid position of the Al atom.

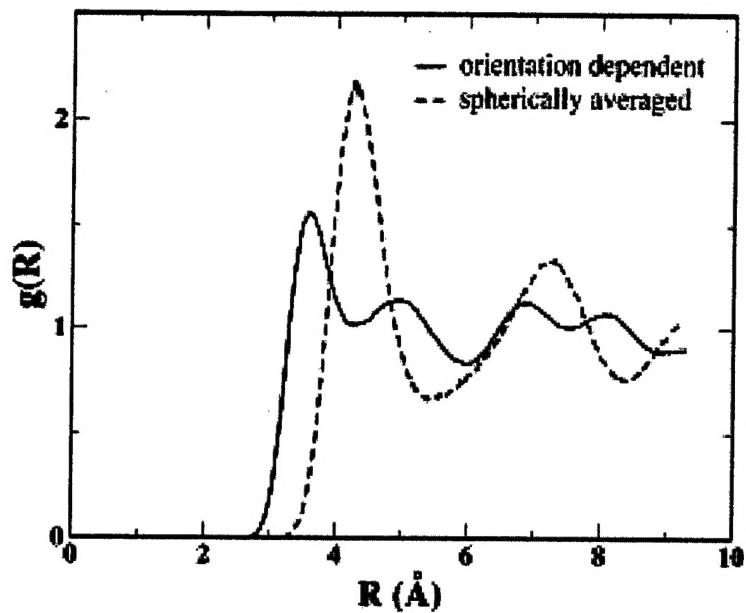


Figure 3

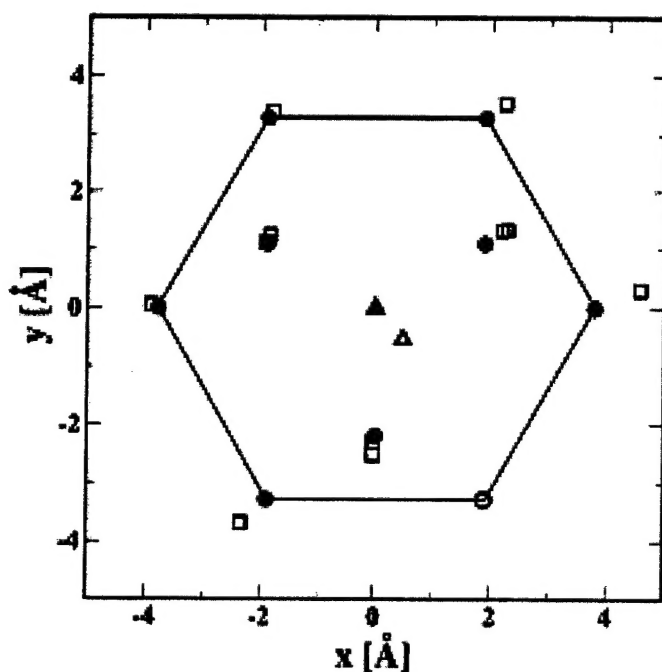


Figure 4

In this case some of the nearest neighbor hydrogen molecules move from their hcp positions, where some stay reasonably close to them. The mean Al atom position shifts, however, slightly towards the vacancy. The projection presented in figure 5 is for the case where the orientation dependent potential was used. In this plot the open circle represents the location of the vacancy. This projection shows that upon equilibration the Al ends up in between its substitution site and the vacancy. There is also evidence that the H_2 molecules shift from their hcp positions slightly

towards the new position of the Al atom. This large shift in position of the Al impurity arises from the strongly anisotropic interaction with the lattice hydrogen molecules.

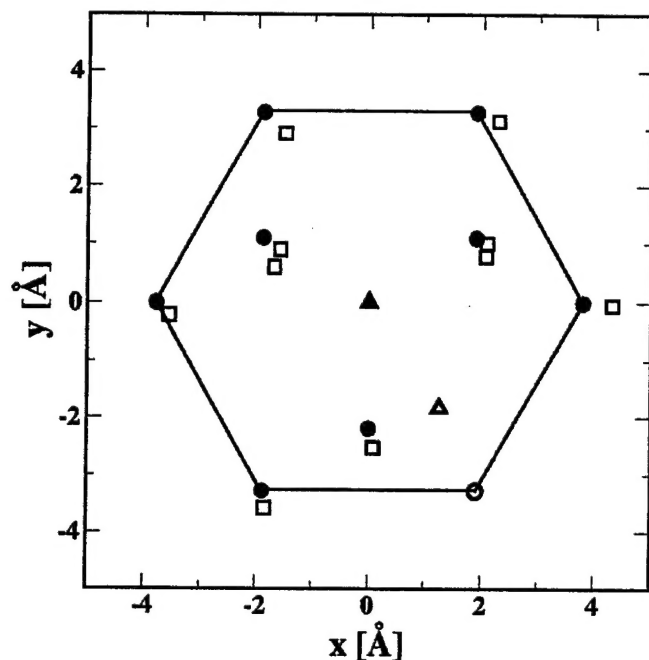


Figure 5

The consequences of the structural details provided above are manifested in the average total impurity- pH_2 interaction energy. These values are listed in Table 1. In all the cases examined here, the orientation dependent potential yields significantly lower (more attractive) average potential energies. The explanation for this remains that orientation dependent Al- pH_2 potential induces some distortion of the nearest neighbor ligand shell to allow the Al p -orbital to orient itself to minimize the repulsive interaction.

The difference in the average potential energy values between the vacancy and the no-vacancy case indicate that the presence of the vacancy helps to stabilize the system, especially when the orientation dependent potential is used. When the spherical potential is used, the difference

System	$\langle V_{Al-H_2} \rangle$ (cm ⁻¹) angle dependent	$\langle V_{Al-H_2} \rangle$ (cm ⁻¹) spherically averaged
Impurity w/o vacancy	-263.41 (3.22)	-177.37 (1.26)
Impurity w/ vacancy	-274.86 (2.37)	-179.52 (1.65)

between the average energies is less than the statistical errors, so that the extent of the stabilization due to the vacancy is unclear. In our previous study with a boron impurity, it was found that the average potential energies for the vacancy and no-vacancy case differed less than the statistical error, both when the orientation-dependent and spherically-averaged potentials were used. Hence, it is clear that when the orientation-dependent potential is used to describe the Al- pH_2 interaction, the embedded Al atom is further stabilized by the presence of a nearest neighbor vacancy.

We continued to work on the determination of the recombination rate of two Al atoms in the solid hydrogen matrix. This was very important, since it allowed us to better assess how good of a candidate Al was for a possible dopant for the HEDM. Constrained path-integral molecular dynamics simulation methods were used to calculate the centroid potential of mean force by varying the centroid of the reaction coordinate from a large value up to where the recombination event occurs. Path-integral quantum transition state theory was then utilized to evaluate the rate constant for the recombination of two Al atoms in the solid hydrogen matrix.

Publications Related to Project:

D. T. Mirijanian, M. H. Alexander, and G. A. Voth, "Path Integral Molecular Dynamics Simulation of Solid *Para*-Hydrogen with an Aluminum Impurity," *Chem. Phys. Lett.* **365**, 487-493 (2002).

J. R. Krumrine, S. Jang, M. H. Alexander, and G. A. Voth, "Quantum Molecular Dynamics and Spectral Simulation of a Boron Impurity in Solid *para*-Hydrogen," *J. Chem. Phys.* **113**, 9079-9089 (2000).

M. G. Del Popolo and G. A. Voth, "On the Structure and Dynamics of Ionic Liquids," *J. Phys. Chem. B* **108**, 1744-1752 (2004).

Interactions/Transitions Related to Project:

(a) Participation/Presentations at Meetings, Conferences, Seminars, etc.

"Anisotropic Impurity-Matrix Interactions Can Be Important in Low Temperature High Energy Density Matter," Air Force Office of Scientific Research Molecular Dynamics Meeting, Irvine, CA, May, 2001.

"Feynman Path Centroid Dynamics: New Concepts and Results," Workshop on Quantum Dynamics in Condensed Phase Systems, Crete, Greece, June, 2002.

(b) Consulting/Advisory Functions

Gaussian, Inc.

(c) Transitions

The parallel CMD computational methodology for cryogenic HEDM has been transitioned to Drs. Jerry Boatz and Jeff Mills of the AF Phillips Lab, Edwards AFB and to Professor Millard Alexander of the University of Maryland (AFOSR Grantee).

New Discoveries, Inventions, Patents:

None

Awards and Honors during Grant Period:

Miller Visiting Professorship, University of California, Berkeley, 2003

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